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**A NEW THEORY FOR THE SHOCK PRODUCTION OF GLASSES AND
HIGH PRESSURE PHASES IN SILICATES**

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Abstract. Recent observation of shock-induced high temperature shear bands, indicate that the high pressure phases of silicates, such as stishovite, crystallize within these bands from melts at temperatures buffered by the melting point of the high pressure phase. This is proposed to be the mechanism of transformation in silicates under shock. Recent shock and static experiments on molten silicates and glasses indicate that these achieve high densities and coordinations via reversible Si-O-Si bond bending. Theoretical calculations quantitatively prescribe, for the first time, the mixed phase region of the Hugoniot of silicates. Fused and crystal quartz upon shocking to 15 and 20 GPa, respectively, transform to a dense, glassy, phase with an entropy of 0.73 R/mole-atom, greater than α -quartz, which has an equation of state similar to stishovite. Transformation to this high density amorphous phase (which rapidly crystallizes to stishovite) is triggered by crossing the metastable extension of the coesite melting curve. This is analogous to formation of super-dense amorphous H₂O-ice upon compression at 77 K through the extrapolation of the ice-I melting curve in the ice-VI field. Shock transformation of mafic silicates are speculated to occur at higher pressures on account of the higher pressures required to achieve local maxima in their melting curves.

Introduction

McQueen et al. [1963] first proposed that the shock wave Hugoniot data then available for SiO_2 (Fig. 1) could be represented in terms of a low pressure phase regime representing the properties of crystal quartz (or fused quartz depending on the starting material), a mixed phase regime and a high pressure phase regime. The latter, representing, the high pressure phase of SiO_2 , stishovite. Shock wave data for all of the other silicates studied and many oxides have similar Hugoniot curves [Ahrens et al., 1969]. Three separate observations suggest that shock-induced phase changes in silicates and oxides occur via the liquid and not the solid state. These observations include: (1) recent pyrospectrometric measurements of shear band temperatures in NaCl , SiO_2 , and $\text{CaAl}_2\text{Si}_2\text{O}_8$ [e.g. Schmitt and Ahrens, 1983; Schmitt and Ahrens, 1988]. The shear band temperatures are consistent with the concept that narrow zones representing shear heated material buffered by the high temperature melting point of the high pressure phase is produced in the mixed phase region [Grady, 1980]. (2) In the range of 0-40 GPa, melts and glasses of silicates continuously and reversibly approach via Si-O-Si bond bending the density and coordination of the close packed oxides [Stolper and Ahrens, 1987; Rigden et al., 1988; Williams and Jeanloz, 1988]. Transitions from crystals to a dense amorphous state can occur upon driving a solid across the negative sloping metastable extension of a fusion curve, as in the case of H_2O [Mishima et al., 1984] and observed more recently in SiO_2 (Fig. 2) [Hemley, 1987; Hemley et al., 1988]. In the present letter I expand an earlier description [Ahrens, 1988] of construction of the Hugoniot in the mixed phase region and the accompanying release isentrope curves for silicates such as SiO_2 . The mixed phase regime is described in terms of a transition to a dense glassy state which in turn crystallizes into the high pressure phase. I propose that

shock-induced reconstructive transformations in other silicates (e.g. MgSiO_3) also occur via the fluid state.

Glassy phases induced by shock pressures in excess of 35 GPa were first recognized in laboratory experiments on quartz [DeCarli and Milton, 1959] and in plagioclase [Milton and DeCarli, 1963]. These results suggested that the shock induced nature of amorphous plagioclase (maskelynite) in the achondrite Shergotty [Duke, 1963], amorphous tecto-silicates from suspected terrestrial impact craters [Dence, 1965], and later shock induced glasses from the moon [von Englehart et al., 1970]. Planar features which contain glass are observed both in nature and from laboratory shock recovery experiments in which silicates were driven into the mixed phase region [Gratz, 1984]. The glass often has a higher than normal index of refraction. Moreover, the sound velocities of silicates shocked to states in this regime immediately unload with the rarefaction velocity corresponding to the bulk sound speed rather than the longitudinal elastic velocity demonstrating that shocked silicates lose their shear strength [Grady et al., 1975], probably as a result of melted material produced in the ubiquitous planar features.

Previously the mixed phase regime was considered to be the result of solid state reactions [e.g. Zamyshlyayev et al., 1982; Jeanloz, 1980]. It was recognized by Ahrens and Gregson [1964] that the transition of quartz to stishovite along the Hugoniot should begin at 7 GPa. Thus the onset of transition is severely overdriven in this and other silicates and in the case of quartz, begins at 15 GPa in fused quartz and possibly as high as 20 GPa along the crystal α -quartz Hugoniot.

Equation of State Model

A key assumption [Ahrens, 1988] is that transformation to a high density amorphous phase

(which rapidly crystallizes to stishovite) is triggered by crossing the metastable extension of the melting curve of coesite as shown in Fig. 2. A consequence of this assumption and the present shock temperature calculations is that the onset of the transition occurs at a lower shock pressure in fused quartz than crystal quartz. Moreover, the metastable melting curve shown goes through the pressures of the onset of transformation in α -quartz and fused quartz, as well as, the pressure range where Hemley [1987] and Hemley et al. [1988] observe amorphization of quartz and coesite. The present model also predicts even lower phase transformation pressures in porous quartz as observed by Ahrens and Gregson [1964]. The onset of the transition is analogous to the transformation ice-I to the super dense amorphous H_2O -ice upon compression at 77 K along a path intersecting the extrapolation of the ice-I melting curve into the ice-VI field [Mishima et al., 1984]. Following the ideas of Zamyshlyayev et al. [1982], I constructed the mixed phase Hugoniot by simultaneously solving three equations for conservation of energy, equality of temperature in both phases, and maximization of entropy

$$\alpha E_1 + (1 - \alpha) E_2 - E = 0 \quad (1)$$

$$(E_1 - E_{s1})/C_{v1} - (E_2 - E_{s2})/C_{v2} + 298[(V_{01}/V_1)^{\gamma_1} - (V_{02}/V_2)^{\gamma_2}] \quad (2)$$

$$(\partial S/\partial \alpha)_E = 0 \quad (3)$$

where E is the fixed internal energy, V , is the specific volume, E_s is the internal energy at volume, V , along an isentrope, γ is the Gruneisen parameter, C_v is the specific volume, and α is the mass fraction of low pressure phase, and S is entropy. Subscripts 1 and 2 refer to low and high pressure phases and subscript 0 indicates the zero pressure value.

An important difference between this procedure and that of Zamyshlyayev et al. is that the

mixed phase regime is not constrained to lie along a line for which the Gibbs free energies of both phases are equal. Moreover, the above expression can only be an approximation to reality as the shear band temperature experiments of Schmitt and Ahrens [1983, 1988] clearly violate the assumption of equation 2. Because thermodynamic and equation of state parameters of Table 1 are only weakly constrained by actual high pressure data, a simple Murnaghan pressure volume isentrope, a constant Gruneisen parameter and specific heat (3R per mole) was assumed. Equations 1-3 represent three non-linear simultaneous equations which are solved for α , V_1 , and V_2 via the Newton-Raphson method. Release isentropes are calculated from the mixed phase Hugoniot down to the stishovite-quartz equilibrium pressure. The mass fraction of unreacted material, α was assumed to be constant. Instead of equations 1 and 3, I used equations 4 and 5.

$$\alpha \left(Es_1 + \frac{(P - Ps_1)V_1}{G_1} \right) + (1 - \alpha) \left(Es_2 + \frac{(P - Ps_2)V_2}{G_2} + E_{TR} \right) - E = 0 \quad (4)$$

$$S = \alpha S_1 + (1 - \alpha) S_2 = \text{constant} \quad (5)$$

where P and P_s are the pressure along the release isentrope and the pressure along the principle isentrope, E_{TR} is the zero pressure phase transition energy. Equations 2, 4, and 5 are solved for P , V_1 and V_2 and these specify the initial portion of the release isentropes for successively lower values of E . Upon reaching the stishovite quartz phase line (at 7 GPa), I allowed the high pressure phase to revert to the low pressure phase. In this case, equations 2, 4, and 5 are supplemented by

$$E - E' + \int_{V'}^V P dV = 0 \quad (6)$$

where the prime indicates a reference energy and volume state. Equations 2, 4, 5, and 6 are then solved for α , V_1 , V_2 , and P .

Results and Conclusions

The high pressure phase produced in the mixed phase regime has an entropy of 0.30 ± 0.02 kJ/kg, greater than that of α -quartz. Transformation to crystal stishovite would give a value of -0.23 kJ/kg which is incompatible with the mixed phase Hugoniot data for both crystal and fused quartz (Fig. 3). The positive entropy gain corresponds closely to the expected value for the entropy of melting ΔS_m which is predicted to vary from 0.28 to 0.41 kJ/kg corresponding to $\Delta S_m = R \ln 2$ to $1R$ per mole [Stishov, 1975]. This is lower than the entropy change inferred by Lyzenga et al. [1983], for the melting of stishovite of $\Delta S_m = 1.3 R$. The fit to the mixed phase regime is much less sensitive to the enthalpy of the high pressure phase. The value given in the Table does not take into account melting, although, if melting enthalpy of 0.13 MJ/kg [Robie et al., 1978] could be added to the high pressure phase value without appreciably changing the fit to the P-V Hugoniot in the mixed phase region. However, taking the larger value of 2.4 MJ/kg inferred by Lyzenga et al. [1983] the theoretical Hugoniot is excessively depressed by as much as 10 GPa at $230 \text{ cm}^3/\text{kg}$. The release isentropes calculated here agree well with previous measurements for quartz shocked into the mixed phase regime [Ahrens and Rosenberg, 1969; Grady et al., 1974; Podurets et al., 1976; and Chhibildas and Miller, 1985].

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Table 1. SiO₂, Equations of State used in Mixed Phase Regimes

Phase	Density (Mg/m ³)	Entropy ^(h) (kJ/kg°K)	Enthalpy ^(h) (MJ/kg)	Bulk Sound Velocity (km/sec)	(dk _s /dP) _s	Gruneisen Parameter
α-quartz	2.648 ^(a)	0.0	0.0	3.77 ^(b)	6.5 ^(b)	0.7 ^(d)
fused quartz	2.203 ^(a)	0.09 ^(a)	0.13 ^(a)	4.00 ^(f)	4.5 ^(f)	1.4 ^(f)
stishovite glass	4.17 ^(c)	0.30 ^(a)	0.83 ^(e)	8.45 ^(g)	3.4 ^(g)	0.9 ^(b)

(a) Robie et al., 1978

(b) Zamyshlyayev et al., 1982

(c) Lyzenga et al., 1983

(d) Anderson et al., 1969

(e) fit to shock data in mixed phase regime

(f) fit to shock data in low pressure phase regime

(g) fit to shock data in high pressure phase regime

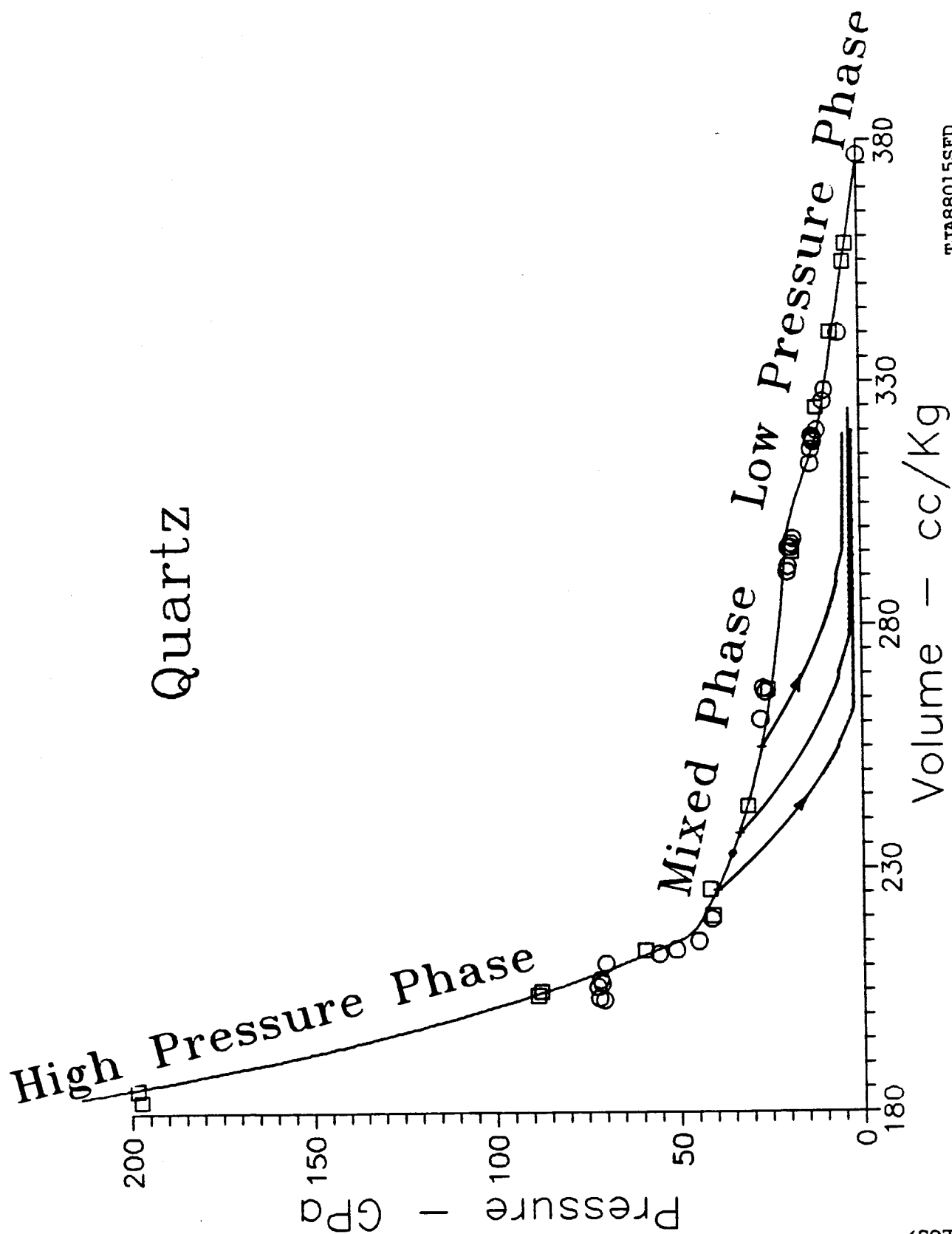
(h) with respect to α-quartz

Figure Captions

Fig. 1. Theoretical Hugoniot curve and release isentropes for crystal quartz. Data, circles, from Wackerle, 1962; squares, Trunin et al., 1971.

Fig. 2. Phase diagram for SiO_2 (after Schmitt and Ahrens, 1988).

Fig. 3. Theoretical Hugoniot and release isentropes for fused quartz. Data circles, triangles, and squares from Wackerle, 1962, Marsh, 1980, and Jones et al., 1968.



SILICA

